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An Introduction to the Revised NR 149 for WWTPs

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Welcome!

This presentation has been modified to eliminate slides not applicable to typical wastewater treatment plant laboratories. If you wish to see the complete version of this presentation, please refer to "An Intro to Revised NR 149- Parts I and II".

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Why Revise NR 149?

- Last substantial revision was in 1994
- Current 149 language conflicts with covered program codes
- Regulated community supported revision of NR149, but not adoption of NELAC

The Department has a statutory obligation to keep current with national trends.

The current version of NR 149 put in same format as the green sheet is roughly 30 pages in length.

Tables in the appendices comprise half of the bulk– the remaining section will be around half of the length when formatted as "code".

We will make available a "Digest" version of the proposed Code. The Digest will highlight requirements for smaller WWTP-laboratories.

Other materials under development include, model benchsheets, sample logsheets, templates for SOPs and the Quality Manual, and guidance for demonstrating sample container cleanliness.

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NR 149 Revision Advisory Committee (RAC)

Laboratory Certification Standards Review Council

Stakeholders

- DATCP
- Environmental Consultant
- Municipal Environmental Group
- WI Environmental Laboratory Association (WELA)
- WI Paper Council

15 Meetings

- Concepts not language for 6 of 7 subchapters
- Quality Systems- interactive development process

RAC meetings started in January 2002 and finished in November 2003

The RAC reviewed the Quality Systems subchapter in detail.

The RAC reviewed a complete draft of the proposed chapter in August 2004.

The RAC directed us to use the good parts of other certification and registration programs, including NELAC, as the basis for modifications.

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NR 149
What Happens Next?

Public Hearings
March 23-April 6 in five cities
Submit written comments by April 14, 2006
Comments compiled and addressed by WDNR
Modifications to current draft, where necessary
Resubmit draft to Natural Resources Board
Legislative review after NRB adoption
Effective date
No sooner than 120 days after legislative approval

Public hearings will be held in:
Eau Claire, March 23
Wausau, March 28
Waukesha, March 29
Green Bay, March 30, and
Dodgeville, April 6.

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"New and Improved NR 149"

7 Subchapters

I. General Provisions
II. Program Administration
III. Program Structure
IV. Certification and Registration Process
V. Proficiency Testing
VI. On-Site Evaluations
VII. Quality Systems

Three Appendices

I. Analytical Techniques, Analytes & Analyte Groups for Certification & Registration in Aqueous and Solid Matrices
II. Methods, Analytes & Analyte Groups for Certification in the Safe Drinking Water Matrix
III. Authoritative Sources

49 pages of the draft are the appendices

The current NR 149, in approximately same format as draft is nearly 30 pages, gives very little specificity for quality assurance and control, and does not identify analytes available for certification or registration.

This proposal is organized topically in subchapters and makes it easier to locate needed information.

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"New and Improved NR 149"

No additional covered programs

Eliminated redundancies

Reorganized- subchapters capture all relevant material to single topic

By consolidating all information related to a single topic navigation of requirements, say for PTs, is now much easier. Previously you had to look in test categories, records, application, renewal, reference samples, enforcement.

Appendices are 49 pages- formerly had to identify each analyte in separate administrative codes for the covered program and guess where it fit in the category structure.

Quality systems is the largest of the subchapters- 24 pages.

On-Site Laboratory Evaluations, our tool for determining compliance, by comparison, is less than 2 pages.

Subchapter I
General Provisions

Key Definitions

Certification
Registration
Certification Matrix
Field of Certification
Field of Registration
Analytical Class
Proficiency Testing Sample
Analytical Instruments
Support Equipment
Preparation Batch
Analytical Batch
Laboratory Control Sample
Second Source Standard

Certification - perform analyses for hire in connection with a covered program, or to laboratories that perform drinking water analyses.
Registration - submits data in connection with a covered program that does not perform analyses for hire and that does not perform drinking water analyses.
Certification Matrix - first tier of a field of certification. Certification matrices are drinking water, aqueous, and solids.
Field of Certification - unit by which the department grants or recognizes certification to a laboratory.
Field of Registration - a unit by which the department grants registration.
Analytical class –a set of analytes of similar behavior or composition, or a set of analytes regulated under the federal safe drinking water act, that is used to organize the third tier of certification or registration.
Proficiency testing sample – "reference samples"
Analytical instruments – any test instrument used to provide analytical results that is not support equipment.
Support equipment - devices that are necessary to support laboratory tests and operations. These devices include autoclaves, balances, ovens, refrigerators, freezers, incubators, water baths, temperature measuring devices, sample preparation devices, and volumetric dispensing devices
Preparation batch – a batch of up to 20 samples, excluding quality control samples, of the same quality system matrix processed in a 24-hour period from the start of the processing of the first sample to the start of the processing of the last sample. A preparation batch may consist of up to 7 samples, excluding quality control , processed during the course of a week in laboratories that do not analyze more than 7 samples for a given test and quality system matrix per week.
Analytical batch - set of any number of prepared samples, or samples requiring no preparatory steps analyzed together as a group in an uninterrupted sequence, and may consist of samples of various quality system matrices.
Laboratory control sample – a sample of an inert matrix fortified with a verified known amount of the analytes of interest, generally used to assess performance
Second source standard – a standard procured from a supplier or manufacturer different from the laboratory's calibration standards, or from a lot verifiably different from the lot of the calibration standards

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Subchapter II
Program Administration

- Consolidates certification program details
- Recognition of other certifications & registrations
- Certification Standards Review Council
- Enforcement
- Discretionary Acceptance
- Variances

Enforcement changes- elimination of automatic NON for proficiency testing failure, all laboratories treated similarly (criteria for enforcement same for registered and certified laboratories).

Much of this language is unchanged, just reorganized.

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Subchapter III
Program Structure

Fields of certification and registration

- Certified laboratory- performs analyses for hire in connection with a covered program requiring certification or registration; SDWA
- Registered laboratory- analyses samples and submits data in connection with covered program for itself, does not perform analyses for hire

The new definitions for certified and registered laboratory now clarify which laboratories are eligible for registration and certification.

Statutory requirements for registration include
Not performing tests commercially for hire, AND
Performing tests solely on its own behalf or on behalf of a subsidiary or other corporation under common ownership or control, OR
Lab is owned or controlled by a municipality or two or more municipalities and performs tests solely on behalf of the municipality or municipalities

Money changing hands is not the sole difference between certification and registration! The code now defines “commercially for hire” as “offering analyses for remuneration or non-monetary compensation generally available to any party requesting analytical services”, which matches current state statutes.

The proposal now clarifies that all SDWA laboratories need to be certified, even if they do not offer analytical services for hire.

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3 Tier Concept

Tier 1- Matrix

- Aqueous- groundwater, wastewater, surface water, biosolids with no more than 15% settleable solids
- Solid- soils, sediments, sludges, and biosolids with greater than 10% settleable solids
- Drinking Water- waters regulated under NR 800 series

Biosolids can be aqueous if the settleable solids are no more than 15%. Overlap is intentional to potentially allow laboratories to analyze biosolids in-house within a single matrix of certification or registration if the laboratory has the capacity to perform these analyses (example might be total solids for landspreading).

It is anticipated that virtually all wastewater treatment plant laboratories will need to maintain certification or registration in the aqueous matrix only.

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3 Tier Concept

Certification Matrices

- Aqueous
- Solids
- Drinking Water

Registration Matrices

- Aqueous
- Solids

Laboratories can be registered or certified in the aqueous and solid matrix. Laboratories can only be certified in the drinking water matrix.

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Tier 2- Analytical Techniques Aqueous and Solid Matrices

- Colorimetric
- Electrometric Assays
- Gravimetric Assays
- Titrimetric or Potentiometric Titrimetric Assays

For the aqueous and solid matrices, the second tier of certification or registration is analytical technique.

These are the typical analytical techniques that might be performed by wastewater treatment plant laboratories.

Note that if a laboratory performs a Winkler titration to calibrate its DO meter, it does NOT need to maintain certification or registration for the titration.

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Tier 3 Analytes & Analyte Groups

- BOD
- Carbonaceous BOD
- Ammonia
- Residue, Filterable (TDS)
- Residue, Nonfilterable (TSS)
- Residue, Settleable
- Residue, Total
- Residue, Volatile (TVS)
- Residue, Volatile, Nonfilterable (TVSS)

The third tier of registration and certification is analyte or analyte group.

These are the typical analytes for which wastewater treatment plant laboratories maintain certification or registration.

We are also offering certification and registration for pH, residual chlorine, and dissolved oxygen, but there is no requirement to be certified or registered to report results of these analyses to the Department. Laboratories can get certified or registered for these analytes voluntarily.

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Fields of Registration
Small WPDES Laboratory

Current NR 149		Proposed NR 149	
		Aqueous Matrix	
Category	**Analyte**	**Analytical Technique**	**Analyte**
01- Oxygen Utilization	BOD Carbonaceous BOD	Electrometric Assays	BOD Carbonaceous BOD
02- Nitrogen	Ammonia as N	Electrometric Assays	Ammonia
03- Phosphorus	Total Phosphorus	Colorimetric or Nephelometric	Phosphorus, Total
04- Physical	TSS	Gravimetric Assays	Residue, Non-filterable

New certificates will look different than the current ones, but the new format will more accurately reflect the analytical capabilities of a laboratory. For instance, we can see from the new structure that this laboratory analyzes ammonia using an ion selective electrode and phosphorus using a spectrophotometer.

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Current Scope
Small WPDES Laboratory

Category 01 – Oxygen Utilization
Biochemical Oxygen Demand
Carbonaceous BOD
Category 02 – Nitrogen
Ammonia as N
Category 03 – Phosphorus
Total Phosphorus
Category 04 – Physical
Total Suspended Solids

This current scope is sent to the laboratory as an attachment to the actual “certificate”.

This laboratory maintains registration for BOD, CBOD, Ammonia, Total Phosphorus and TSS.

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Post-Revision Scope
Small WPDES Laboratory

Aqueous Matrix
Electrometric Assays
Biochemical Oxygen Demand
Carbonaceous BOD
Ammonia
Colorimetric or Nephelometric
Phosphorus, Total
Gravimetric Assays
Residue, Nonfilterable

The post-revision scope identifies the matrix (aqueous), analytical techniques (electrometric assays, colorimetric or nephelometric, and gravimetric assays) and the corresponding analytes for which this laboratory maintains registration.

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Analyte Classes
Aqueous & Solids

- Demand
- Nutrients
- Physical

Analytical classes organize all the possible analytes for which laboratories can obtain certification or registration in the aqueous and solids matrices into “affinity” sets.

Analytical classes mirror those used by PT providers.

The analytical classes for routine wastewater treatment plant analytes:
Demand includes: BOD, COD, TOC
Physical includes: Filterable Residue, Nonfilterable Residue, Oil & Grease, HEM
Nutrients includes: Ammonia, TKN, Nitrate, Nitrite, Total Phosphorus

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Subchapter IV
Certification & Registration Process

Applications
- Initial
- Revised
- Transfer of certifications or registrations
- Reciprocity
- Renewal

Relocation

Laboratory Name Change

This subchapter is where laboratories would go to obtain information on how to apply to the program and how much it would cost to obtain or maintain certification and registration.

Applications
Initial – a complete inventory of analytes and analytical techniques for which a laboratory seeks certification or registration. At the time the revision become effective, a shortened version of an initial application will be required of all laboratories.
Revised – not much change from the current practices; used for minor changes
Transfer of certification or registration – used when the Department determines that existing certifications or registrations can be transferred to a new owner; otherwise, an initial application is required.
Renewal – annual application to update contacts and inform of changes in personnel, methods within a certified or registered technique, or laboratory equipment; will be electronic and if no changes have occurred, will be a simple verification. There is no fee assessed for the annual renewal application.

The Code now outlines a process that laboratories need to follow when they move. The Department may perform an on-site evaluation at the new location.

Laboratories that change their name without a change in ownership or scope of certification or registration will be issued a new certificate at no cost.

We are catching up with rest of DNR with electronic reporting (EDMR, CMAR, DW) and plan to automate the application process electronically as much as possible.

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Fees

Annual Spending Authority set by DOA

No increase in staffing

Fee formula unchanged

More equitable distribution of RVUs

RVUs are relative value units. The number of RVUs assigned to a technique, application, or class is directly related to the complexity of the task or the anticipated effort necessary to review any of them during an evaluation. This is not a new concept. Currently, fees are assessed on the same principle.

Because of the way the new scopes of certification and registration have been constructed, there are more number of RVUs available to recover program costs. More RVUs for the entire program means that the cost of an RVU will be lower.

Our projections show that fees will not change significantly for most laboratories. Some laboratories will see slight decreases in their fees and some small drinking water laboratories may experience more substantial decreases.

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Proposed Annual Fees Aqueous & Solid Matrices

Base Fees

- Certification: 10 RVU
- Registration: 5 RVU
- Minimum Annual Certification Fee: 24 RVU

Matrix Fees

- Aqueous: 5 RVU
- Drinking Water: 5 RVU
- Solids: 5 RVU

Analytical Technique Fees

Matrix fees are now assessed under the new proposal. However the sum of the base fee and matrix fee for a laboratory certified or registered for a single matrix under the proposal exactly equals the current base fees for certification and registration.

The program will continue to assess a minimum annual certification fee but now includes exemptions from the fee for certified laboratories analyzing a set of typical wastewater analytes.

The proposal, as is also the case with the current code, does not assess a minimum fee to any registered laboratory.

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Analytical Technique Fees Aqueous & Solid Matrices

Analytical Technique	RVU
Colorimetric or Nephelometric Spectrophotometry	2
Electrometric Assays	1
Gravimetric Assays, Residues	1
Titrimetric or Potentiometric Titration Assays	1

Fees are assessed by analytical technique for the aqueous and solid matrices. Within a certified or registered analytical technique, a laboratory can add any analytes appropriate for the technique without having to pay additional fees.

The number of RVUs assigned to a technique is based on the complexity of the analytical technique. The specific values assigned were based on a survey that asked RAC members and laboratory certification program staff to rate the relative complexity of analytical techniques.

The analytical technique fees for routine wastewater treatment plant laboratories.

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Fees
Small WPDES Laboratory

Current Fees	RVU
Registration Base Fee	10
Category 01- Oxygen Utilization	1
Category 02- Nitrogen	1
Category 03- Phosphorus	1
Category 04- Physical	1
Total:	**14**
Proposed Fees	**RVU**
Base Fee, Registration	5
Matrix Fee, Aqueous	5
Technology Fees:	
Colorimetric or Nephelometric	2
Electrometric Assays	1
Gravimetric Assays	1
Total:	**14**

Note that the RVUs for a typical small wastewater treatment plant laboratory are not increasing as a result of this proposal.

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Proposed Application Fees

Type	Current	Proposal
Initial	6	6
Revised	3	3
Reciprocity	30 *	4
Transfer of Ownership	4	4

* Flat fee includes application and certification

The proposal does not change the fees for other types of applications.

There is no fee for the annual renewal application.

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Proposed Administrative Fees

Type	Currently	Proposal
Discretionary Acceptance	Actual Cost	Actual Cost
Evaluation Cancellation		Incurred
Evaluation for Enforcement Follow-Up	Actual Cost	Actual Cost
Evaluation of Out-of-State Labs	Actual Cost	Actual Cost
Late Renewal Fee	2	2

The code proposal allows us to recover any incurred costs for cancelled out of state audits.

The late renewal fee is not proposed to change with this revision.

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Subchapter V
Proficiency Testing

- Time frame for analysis: 9/1 to 8/15
- Annual list of available PTs published by WDNR
- Key analytes are gone, now analyte by analyte
- Kept it simple for multiple techniques

The proposal allows laboratories to analyze a PT from September 1 to August 15 of the following year to qualify for renewal of certifications and registrations.

The current proposal does not use key analytes, but allows laboratories to use the same PT for multiple analytical techniques for analytes in the aqueous matrix (such as BOD and CBOD).

PTs are required to undergo the preparatory steps of the analytical procedures performed at the laboratory.

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Aqueous Matrix
Proficiency Testing Failure

Analyze second PT sample

Failure PT #2

- Submit corrective action report
- Initiate action plan
- Analyze third proficiency testing sample

Failure PT #3

- Will not be renewed, unless
- Analyze & pass 2 successive PTs

The proposal eliminates the automatic enforcement for multiple proficiency testing failures for certification or registration in the aqueous matrix. Instead of receiving a Notice of Noncompliance (NON), laboratories will not be renewed for the affected techniques, unless they pass the third PT.

Laboratories that fail the third PT, must successfully analyze 2 consecutive PTs.

Note that in the language style used for administrative codes, “may not” is the opposite of “shall”. The “Department may not” means “the Department will not”.

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Required PTs
Small WPDES Laboratory

Aqueous Matrix

Electrometric Assays

Biochemical Oxygen Demand	WP
Carbonaceous BOD	WP
Ammonia	WP

Colorimetric or Nephelometric

Phosphorus, Total	WP

Gravimetric Assays

Residue, Nonfilterable	WP

This identifies the commonly available types of PT for the listed analytical techniques. To obtain certification for CBOD laboratories will now have to analyze a PT. However, the same PT that is analyzed for BOD can be also analyzed for CBOD.

Using key analytes created some confusion and made some laboratories analyze for a test they never would perform just to obtain certification or registration for a different analyte in the same test category, as for example, when a laboratory had to analyze a hardness sample to obtain certification or registration for bromide. The code proposal establishes a more direct link between certified and registered analytes and PTs.

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Subchapter VI
On-Site Evaluations

- 3-year interval
- Laboratory relocation can trigger audit
- Specifies timeframes for WDNR and laboratory responses
- Conflict of interest

This is the shortest subchapter in the proposed code.

The frequency of on-site evaluations remains the same. The proposal specifies deadlines the Department will meet to issue reports and close open cases and requires the Department to establish procedures to prevent conflicts of interest for evaluators assigned to participating laboratories.

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Subchapter VII
Quality Systems

- General Requirements
- Laboratory Personnel
- Quality Manual
- Corrective Action
- Records and Documents
- Standard Operating Procedures
- Method Selection
- Alternative Methods
- Laboratory Facilities
- Laboratory Equipment
- Measurement Traceability
- Handling of Samples
- Laboratory Test Reports
- Quality Control Requirements for Chemical Testing
- Quality Control Requirements for Whole Effluent Toxicity Testing

The Quality Systems subchapter constitutes the core of the code proposal. It is the longest subchapter in the revision.

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Personnel Requirements

- Only as specified for drinking water
- No formal education or experience for other testing
- Now explicit that all analysts have to demonstrate proficiency

The proposal does not require specific training, education, or experience, except as specified for analysts analyzing drinking water. Instead, the proposal relies on demonstrations of capability to show that whatever training, education or experience an analyst has allows him or her to perform required analyses competently.

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Initial Demonstration of Capability

- Determines adequate performance
- Grandfathering existing laboratory staff
- Analyst can work under supervision until IDC
- Many laboratories already performing training that meets this definition

The code proposes to grandfather existing laboratory staff if they can document acceptable results for four quality control samples analyzed in year prior to new code's effective date. Four quality control samples can be four laboratory control samples, four matrix spikes, four replicates, four PTs, four blinds or a combination of any of these yielding four valid results.

If an analyst does not meet the grandfathering criteria, then they must successfully analyze either four quality control samples "blinds", 4 laboratory control samples, or 4 matrix spikes. The average recovery must be 50-150% and the standard deviation <33.

For tests for which fortifying (spiking) samples is not possible, attesting that personnel have read and can meet the specifications of the test's SOP serves as an IDC.

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Documentation Policies & Procedures

Quality Manual
- Content elements specified
- Flexible format
- Templates to be available

SOPs
- Analytical and non-analytical procedures
- Analytical methods manual is a subset of SOPs
- Content elements specified
- Flexible format
- Templates to be available

The Department believes that the Quality Manuals of most laboratories meet the requirements of the proposed code. The proposal allows flexibility in the format of the Manual.

The Analytical Methods Manual is a subset of the Standard Operating Procedures (SOPs) laboratories may need to maintain. The Analytical Methods Manual may consist of
Copies of published procedures
Copies of published procedures complemented by writing modifications made to the original source.
Standard Operating Procedures written by the laboratory addressing elements specified in the revision.

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Laboratory Analytical Records

Minimum Retention = 5 years

Ensure Permanence

Specific provisions for electronic recordkeeping

Administrative
- Copies of certificates
- Personnel qualifications, if specified elsewhere

Analytical & technical- "raw data"

Reports

This proposal increases the record retention minimum to five years to reflect current best practices. Water supplies must retain records for ten years and hazardous waste facilities must retain them for the life of the operation. DMRs currently may be required to be kept for five years.

The proposal specifies in NR 149.47 the content elements of reports issued to the Department and to clients. When laboratories report results to internal clients or use forms mandated by the Department for reporting results, the content elements may not all be included in the issued reports. However, upon request by the Department, the laboratory must provide records containing the specified information.

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Measurement Traceability

- Reagent origin, purity, track pedigrees
- Standard and reagent preparation
- Templates and forms available from WDNR

"Measurement traceability" is the industry term for describing the process of connecting reported results to the reagents and standards used to derive or obtain the results. Many laboratories are already documenting this information. The Department will provide templates and forms for those laboratories that may need assistance managing this information.

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Handling of Samples

- Distinguishes between responsibilities of collector and laboratory
- Preservation required within 15 minutes
- Temperature from above freezing to 6º C

The proposed code makes a clearer separation between sample collection activities and laboratory responsibilities. Because NR 149 applies to laboratories, the proposal assigns requirements to processes and procedures applying to laboratories. It is true, however, that many laboratories are intimately connected with sample collection operations. The proposed code assumes that even when the same personnel is responsible for collecting and analyzing samples, it is possible to segregate sample collection events from analyses. Sample collectors are responsible for collecting and preserving samples. Laboratories are responsible for verifying the condition of samples on receipt and for determining whether received samples meet preservation requirements.

When samples will be delivered to the laboratory within 15 minutes of collection, the collector does not have to preserve samples chemically or thermally if the laboratory performs the necessary preservations, or starts analysis, within 15 minutes of collection. Sample collectors must preserve samples that reach the laboratory later than 15 minutes after collection. In these cases, the laboratory is responsible for determining sample condition upon arrival.

The 15-minute preservation time limit is referenced in NR 219 for WPDES-facilities and in the fifth edition of the "Manual for the Certification of Laboratories Analyzing Drinking Water".

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Sample Acceptance Policy

- Assists laboratory in ensuring sample integrity
- Guidance to be developed by program
- Includes directions on how to determine sample condition

The proposal requires laboratories to document the conditions under which they accept samples and what steps they will take when a sample is received that does not meet the laboratory's policies. Laboratories that analyze drinking water samples will be required to state that they will reject samples for analysis that are not properly preserved or will proceed with analyses if directed to do so, but will flag all results as not valid for determining compliance with the Safe Drinking Water Act.

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Container Cleanliness Protocols

Essential to ensuring sample integrity

Includes

- Carboys for autosamplers
- Individual sample bottles
- Preservatives added to samples in field

Can be documentation from manufacturer

WDNR to provide guidance

When laboratories supply, as is customary, containers for sample collection, the laboratory must ensure that the provided containers are free of the analytes of interest and that any added preservatives will not contaminate samples. The Department will provide guidance on how to perform protocols for determining the cleanliness of collection bottles.

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Laboratory Support Equipment

Routine and preventative maintenance

Calibrated or verified over range to NIST-traceable reference materials

- Thermometers
- Class I weights

Remove from service if out of specification

- Can use if consistent bias, with applied correction factor

Support equipment means devices that may not be analytical instruments but that are necessary to support laboratory tests and operations. These devices include, but are not limited to, autoclaves, balances, ovens, refrigerators, freezers, incubators, water baths, thermometers, and pipets.

A thermometer that consistently read below or above a true temperature can be used if a correction factor is determined and used to adjust the thermometer's reading.

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Support Equipment Calibration or Verification

Equipment	Method	Frequency
Thermometers, thermocouples, infrared guns	NIST-traceable thermometer	Yearly
Analytical balances	NIST-traceable weights- 1 gm range, 1 mg range	Monthly
Non-analytical balances	NIST-traceable or verifiable- range of use	Monthly
Mechanical and automatic micro-pipettes, burets, dilutors and dispensers	Verify volume transferred gravimetrically	Quarterly
Volumetric glassware and syringes, Class A		Exempted
Disposable pipettes, used in method steps		Exempted

This summarizes the method and frequency for calibrating or verifying support equipment. Note that these procedures would not apply to analytical instruments such as spectrophotometers.

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Sample Testing and Holding Calibration or Verification

Equipment	Criteria	Frequency
Refrigerators for sample storage	Above freezing to 6° C	Daily, when in use
Thermostats to be set so that temperature is maintained on days samples are stored		
Autoclaves, incubators, ovens & water baths for sample processing	Method-specified	Daily, when in use
BOD incubator thermostats to be set so that temperature is maintained on days samples are processed		

This summarizes the criteria used for determining the calibration state of support equipment that holds samples and the frequency of the verification. The proposal does not require laboratory personnel to monitor the temperature of refrigerators and incubators on days when personnel are not scheduled to be present to perform analyses.

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Laboratory Analytical Instruments

- Calibrated at least annually
- Calibrated or calibration verified before use
- Preventive and routine maintenance

Analytical instruments are instruments that are not support equipment and that are used to provide analytical results. Spectrophotometers, ISEs, GCs, AAs, and ICPs are all examples of analytical instruments.

The following slides summarize the procedures used to calibrate and verify the calibration of analytical instruments.

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Initial Calibration

Defer to analytical method if more stringent

Calibration model

- Appropriate for behavior of instrument
- Concentration range to encompass expected sample concentrations
- Linear, quadratic, cubic

Acceptability

- Correlation Coefficient
- Coefficient of Determination
- RSD

To establish an initial calibration, a laboratory would:
Choose an appropriate calibration model.
Select a number of standards to establish the calibration that is suitable for the model chosen.
Establish the concentration of each of the standards required by the model.
Choose a reduction technique or algorithm that is appropriate to the model.
Establish acceptance criteria for the calibration.

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Initial Calibration

Number of Standards

Acceptability Criteria

Special Cases

- pH Meter
  - pH = 2 buffers
- DO Probe
  - Air-saturated water to established calibration point
  - Water-saturated air to established calibration point
  - Winkler or iodometric titration
- Ion Selective Electrodes
  - 2 standards, minimum

The minimum number of standards to establish an initial calibration is:
Three, for linear models.

The acceptability criteria for some reduction techniques:
Linear regression, inorganics: $R \geq 0.995$

For pH meters, it is customary to use a neutral pH buffer of 7 and another one at a pH of 2, 4, 10, to bracket the expected values of samples.

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Initial Calibration Verification

Different source from calibration standards

Analyzed immediately after initial calibration, unless:

- Exempted by universal law (DO, pH, ISE)
- QCS analyzed 3/year

Acceptance criteria for ICV same as continuing calibration verification

Immediately after establishing an initial calibration, its validity must be verified with a standard from a source different than the one used for the initial calibration. This standard is called initial calibration verification (ICV) standard.

Laboratories that analyze known Quality Control Samples (what the current code calls blind standards) three times per year do not have to analyze ICVs.

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Continuing Calibration Verification (CCV)

- At beginning of analytical batch when no initial calibration
- Analyzed at end of analytical batch "closing CCV", except:
  - When using next analysis day opening CCV
- Analyzed after 20 samples, if >20 samples in analytical batch
- Default acceptance criteria
  - ± 10% for inorganic analytes

A continuing calibration verification standard (CCV) is the equivalent of the "known standard" currently analyzed for phosphorus.

CCVs are used to determine whether an initial calibration is still valid. The source of the CCV is the same as the source used to prepare the calibration standards.

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Continuing Calibration Verification (CCV)

Number to be analyzed:
- 1, when initial calibration is linear

CCV Failure

Second CCV Failure

DO analysis is a special case and does not require analysis of a CCV.

When a CCV fails, a laboratory must analyze a second CCV. If the second CCV fails the laboratory must take corrective action and recalibrate unless 2 consecutive CCVs after taking the corrective action pass.

When a calibration cannot be verified all associated samples must be reanalyzed except that:
When a calibration cannot be verified because the CCVs are high, analytes that are not detected in samples may be reported with appropriate qualifiers.
When a calibration cannot be verified because the CCVs are low, analytes exceeding a regulatory limit or decision level in samples may be reported with appropriate qualifiers.

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Quantitation

- From initial calibration only
- Retain all data necessary to reconstruct quantitation event

Access to raw data is necessary to reconstruct all calibration functions.

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Quality Control Elements

- Limits of Detection and Quantitation
- Method Blanks
- Laboratory Control Samples
- Matrix Spikes and Matrix Spike Duplicates
- Sample Replicates
- Quality Control Samples

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General Provisions

Spiking material from different source than initial calibration, unless Quality Control samples analyzed

Frequency tied to preparation batch (or analytical batch if no preparative step)

Quality system matrices:

- Wastewater Influent
- Wastewater Effluent
- Biosolids

Quality system matrices are used to establish quality control acceptance criteria. Quality system matrices are not the matrices used for certification or registration, but are of course, related. A laboratory certified or registered in the aqueous matrix could be analyzing wastewater influents and effluents, and biosolids with no more than 15% settleable solids.

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Limits of Detection and Quantitation

- Procedure
- Frequency
- Exemptions
- Procedure to relate LOQ to LOD

This proposal does not require a specific method for determining LODs and LOQs and defers to other regulations. The MDL procedure is referenced in many approved methods and in some regulations, but it is not the only acceptable procedure for determining detection limits.

The following tests and analytical techniques are exempted from the LOD requirement:

- BOD.
- Gravimetric except HEM.
- Titrimetric.
- Tests for which one cannot spike with a standard.

Laboratories need to establish procedures for relating LODs to LOQs, but the proposal does not require a specific method for doing this.

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Method Blank

- Processed under same conditions and steps as samples
- Frequency
- Data acceptance, reanalysis and qualification

Samples in a batch must be reanalyzed or qualified if the concentration of analyte of interest in a method blank exceeds the highest of:

- the LOD.
- 5% of the regulatory limit for the analyte.
- 10% of the measured concentration in a sample.

The current code uses 5% of the measured concentration in a sample as the third level for the trigger for qualifiication.

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Laboratory Control Samples

- "Second Source"
- Frequency
- LCS for BOD is GGA
- Exemptions

Laboratory control samples (LCS) are used to assess the level of control an analysis. The standards used to prepare them are from a source different from the source of the calibration standards, unless the laboratory analyzes known quality control samples (formerly blind standards) three times per year.

The LCS for BOD is GGA.

Tests exempted from LCS requirement are:

- pH
- All solids determinations, that is, tests to determine solids content, not all tests performed on the solid certification or registration matrix.
- Chlorophyll a
- Color
- Odor
- Oil and Grease as freon extractable material

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Laboratory Control Samples

- Substitution of matrix spikes or certified reference materials
- Laboratory to compute recovery of each fortified analyte
- Control limits
- LCS Failures

Laboratories can use matrix spikes in place of LCS if matrix spikes are assessed against control limits for LCS.

LCS must be fortified with all reported analytes.

Control limits for LCS are:

- Established by the Department
- Contained in approved methods of analysis
- Generated from in house data when the former two conditions are not met.

LCS failure requires reprocessing, reanalyzing or qualifying all associated samples.

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Matrix Spike & Matrix Spike Duplicates

Required

- When specified by method
- In project plans, client agreements
- As a substitute for Laboratory Control Samples

Processed with and under same conditions as samples

The current proposal de-emphasizes matrix spikes. Matrix spikes are required if specified by a method, project plan, or client, and if they are used instead of LCS. When matrix spikes are used in place of LCSs, the matrix spikes must be fortified with all reported analytes.

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Matrix Spike & Matrix Spike Duplicates

Frequency

- One per preparation batch and quality system matrix

Calculations

- Compute recovery for all fortified analytes and RPD for MS/MSDs

Control limits

- Established by DNR, from method or in-house

Failure

- Reanalyze or reprocess
- Qualification of data

Control limits for MS and MSDs are:
Established by the Department
Contained in approved methods of analysis
Generated from in house data when the former two conditions are not met.

Matrix spike failures require reprocessing, reanalyzing, or qualifying the sample chosen for fortification. When a matrix spike is used in place of an LCS failure requires reprocessing, reanalyzing or qualifying all associated samples.

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Sample Replicates

Can be substituted for Matrix Spike Duplicates

Required

- When specified by method
- In project plans or specified by client

Processed with and under same conditions as samples

Sample replicates can be used in place of matrix spike duplicates when there is a high probability that replicates will contain the analytes of interest.

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Sample Replicates

- Frequency
  - One per preparation batch and quality system matrix
- Calculations
  - RPD or range
- Control limits
  - Established by DNR, method or in-house
- Failure
  - Reanalyze or reprocess
  - Qualification of data

Control limits for replicates are:
Established by the Department
Contained in approved methods of analysis
Generated from in house data when the former two conditions are not met.

Replicate analysis failures require reprocessing, reanalyzing, or qualifying the sample chosen for fortification.

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MSD or Sample Replicate?

- Matrix spike duplicate ensures analyte present
- MSD required if <LOQ
- Replicate OK, if know analyte is there
- Inherent risk unless know sample concentrations consistent

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Quality Control Samples

- Required if not using second source standard to verify initial calibrations (ICVs)
- Required if not using second source standard to fortify LCS, MS, MSD
- Frequency
- Control limits established by provider
- Corrective action and addressing failures

These are what the current code calls blind standards. Laboratories that use ICVs and that fortify quality control samples with second source standards do not have to analyze QCSs.

Laboratories that do not analyze second source standard must analyze QCSs three times per year at approximately evenly spaced intervals.

When a QCS fails, a laboratory must take corrective action and analyze another QCS or a second source standard within 30 days to demonstrate that the corrective action was effective.

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Example #1

Analytical Test: Colorimetric Total Phosphorus

Calibration routine: 3 standards, Linear

Analytical batch: 12 samples, digested in 2 preparation batches

This example illustrates what the laboratory would do on a day when it is performing an initial calibration.

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Example #1
Phosphorus with Initial Calibration

Standard 1, source A

Standard 2, source A

Standard 3, source A

Initial Calibration Verification, source B

Method Blank 1 (from preparation batch 1)

Laboratory Control Sample 1 (preparation batch 1), source B

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Example #1
Phosphorus with Initial Calibration

Samples 1-6

Continuing Calibration Verification standard, source A

Method Blank 2 (from preparation batch 2)

Laboratory Control Sample 2 (preparation batch 2), source B

Samples 7-12

Closing Continuing Calibration Verification standard, source A

63	**Example #1, Phosphorus with Initial Calibration, Summary** 1-3. 3-point Calibration Curve, source A 4. ICV, source B 5. MB 1 6. LCS 1 source B 7-12. Samples 1-6 13. CCV, source A 14. MB 2 15. LCS 2, source B 16-22. Samples 7-12 23. Closing CCV, source A	If the laboratory analyzes QCS, the ICV can be eliminated. If the laboratory analyzes matrix spikes and evalutes them against the acceptance criteria for Laboratory Control Samples, the LCS can be eliminated. Analysis of MS/MSD or replicates is only required if specified by method and there is sufficient sample volume to do it.
64	**Example #1** **Phosphorus Without Calibration** Continuing Calibration Verification standard, source A Method Blank 1 (from preparation batch 1) Laboratory Control Sample 1 (preparation batch 1), source B Samples 1-6 Continuing Calibration Verification standard, source A	This example illustrates what the laboratory would do on a day when it is not performing an initial calibration.
65	**Example #1** **Phosphorus Without Calibration** Method Blank 2 (from preparation batch 2) Laboratory Control Sample 2 (preparation batch 2), source B Samples 7-12 Closing CCV standard, source A	

66	**Example #1 Phosphorus Without Calibration, Summary** 1. CCV, source A 2. MB 1 4. LCS 1, source B 5-10. Samples 1-6 11. CCV, source A 12. MB 2 13. LCS 2, source B 14-19. Samples 7-12 20. Closing CCV, source A	If the laboratory analyzes matrix spikes and evalutes them against the acceptance criteria for Laboratory Control Samples, the LCS can be eliminated. Analysis of MS/MSD or replicates is only required if specified by method and there is sufficient sample volume to do it.
67	**Example #2** Analytical Test: Ion Selective Electrode Ammonia Calibration Routine: 3 standards, Linear Curve log [standard concentration] v. mV response Analytical Batch: 6 samples, undistilled	Because ion selective electrodes require daily calibration, this is what the proposal requires for ammonia analysis.
68	**Example #2 Ammonia Initial Calibration** 0.2 mg/L standard, source A 2.0 mg/L standard, source A 20 mg/L standard, source A Method Blank Laboratory Control Sample, source B Samples 1-6 Closing Continuing Calibration Verification standard, source A	

69	**Example #2, Ammonia Initial Calibration, Summary** 1-3. 3-point Calibration, source A 4. MB 5. LCS, source B 6-11. Samples 1-6 12. Closing CCV, source A	If the laboratory analyzes matrix spikes and evalutes them against the acceptance criteria for Laboratory Control Samples, the LCS can be eliminated.
70	**Example #3** Analytical Test: BOD Calibration Routine: DO Meter calibrated each day of use with water-saturated air Analytical batch: 2 influents, 2 effluents plus seed controls	
71	**Example #3 BOD** Method Blank (dilution water) LCS (glucose-glutamic acid) Seed control (minimum 2 dilutions) Influents 1 and 2 Effluents 1 and 2	DO meter calibrated using water-saturated air; laboratory records temperature, barometric pressure and resulting calibration value.

7
2

Example #3, BOD, in summary

1. Standardize DO Meter
2. MB
3. LCS (GGA)
4-5. Seed Controls
6-9. Samples 1-4s

7
3

Example #4

Analytical Test: Solids, Nonfilterable (TSS)

Calibration Routine: Analytical balance verified monthly in gm- and mg-range

Analytical batch: 1 influent, 1effluent

7
4

Example #4 Nonfilterable Residue Balance Verification & Procedure

Balance verified with Class I weights in gm and mg-range monthly

Filter tare weights determined

Samples filtered and dried overnight at 103-105º C

Final weights determined

Results calculated

Test does not require method blanks, laboratory control samples or spikes. Replicates are only required by method or client request.

Because the laboratory dries samples overnight, it only verifies the constant weight of samples once a quarter, as currently allowed. On this analysis day, the laboratory did not have to perform the constant weight verification.

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Example #4
Nonfilterable Residue Summary

1-2. Verify Analytical Balance to gm, mg-range

3-4. Determine tare weights

5-6. Filter samples and dry

7-8. Determine captured weight

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Phosphorus Analysis Now

Colorimetric Total Phosphorus

Calibration: 3 standards, Linear

Analytical Batch: 6 samples, digested in a single preparation batch

The following slides illustrate what is required of phosphorus analysis now.

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Phosphorus Analysis Now
Day of Initial Calibration

Initial Calibration

3 Standards, R= 0.998

Method Blank

Samples 1-6

Sample 1 Replicate

Sample 1 Matrix Spike

** Laboratory analyzes "Blinds" 3 times/year

78	**Do I need to change?** **No, if:** 1. Laboratory continues to analyze Quality Control Sample for test three times per year. 2. Matrix Spike is assessed against control limits for Laboratory Control Sample 3. Continuing Calibration Verification standard analyzed with the next batch is acceptable	A laboratory can continue to analyze phosphorus without purchasing a second source standard, and without processing an LCS, an ICV, and a closing CCV if it meets the conditions illustrated in this slide.
79	**Phosphorus Analysis Now Calibration Verification** Colorimetric Total Phosphorus Calibration: Verification of Calibration with "Known Standard" Analytical Batch: 6 samples, digested in a single preparation batch	This illustrates what a laboratory does now for phosphorus analysis on a day when it does not perform a calibration.
80	**Phosphorus Analysis Now Calibration Verification** Known Standard Method Blank Samples 1-6 Sample 1 Replicate Sample 1 Matrix Spike ** Laboratory analyzes "Blinds" 3 times/year	The known standard is acceptable if recovery is 90-110%.

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Do I need to change?

No, if:

1. Laboratory continues to analyze Quality Control Samples for test 3 times/year
2. Matrix Spike is assessed against control limits for Laboratory Control Sample
3. Continuing Calibration Verification standard analyzed with the next batch is acceptable

On a day when a calibration is not performed, a laboratory can continue to analyze phosphorus without purchasing a second source standard, and without processing an LCS and a closing CCV if it meets the conditions illustrated in this slide.

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An Even Better Option…

- Analyze Matrix Spike/Matrix Spike Duplicate to ensure results >LOQ
- Reread Continuing Calibration Verification standard (CCV) at end of analytical sequence to minimize potential for data qualification

The same CCV standard read at the beginning of the analysis run can be read as the closing CCV, assuming that the lag in time does not affect the standard's response.

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Feel free to contact any of us with your questions about this presentation or the proposed revision to Chapter NR 149.